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Investigation on Mn_3O_4 Coated Ru Nanoparticles for Partial Hydrogenation of Benzene towards Cyclohexene Production Using ZnSO_4 , MnSO_4 and FeSO_4 as Reaction Additives

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Abstract: Mn_3O_4 coated Ru nanoparticles ($\text{Ru@Mn}_3\text{O}_4$) were synthesized via a precipitation-reduction-gel method. The prepared catalysts were evaluated for partial hydrogenation of benzene towards cyclohexene generation by applying ZnSO_4 , MnSO_4 and FeSO_4 as reaction additives. The fresh and spent catalysts were thoroughly characterized by XRD, X ray fluorescence (XRF), XPS, TEM and N_2 -physicalsorption in order to understand the promotion effect of Mn_3O_4 as the modifier as well as ZnSO_4 , MnSO_4 and FeSO_4 as reaction additives. It was found that 72.0% of benzene conversion and 79.2% of cyclohexene selectivity was achieved after 25 min of reaction time over $\text{Ru@Mn}_3\text{O}_4$ with a molar ratio of Mn/Ru being 0.46. This can be rationalized in terms of the formed $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ on the Ru surface from the reaction between Mn_3O_4 and the added ZnSO_4 . Furthermore, Fe^{2+} and Fe^{3+} compounds could be generated and adsorbed on the surface of $\text{Ru@Mn}_3\text{O}_4$ when FeSO_4 is applied as a reaction additive. The most electrons were transferred from Ru to Fe, resulting in that lowest benzene conversion of 1.5% and the highest cyclohexene selectivity of 92.2% after 25 min of catalytic experiment. On the other hand, by utilizing MnSO_4 as an additive, no electrons transfer was observed between Ru and Mn, which lead to the complete hydrogenation of benzene towards cyclohexane within 5 min. In comparison, moderate amount of electrons were transferred from Ru to Zn^{2+} in $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ when ZnSO_4 is used as a reaction additive, and the highest cyclohexene yield of 57.0% was obtained within 25 min of reaction time.

Keywords: Ru; Mn_3O_4 ; benzene; cyclohexene; additives

1. Introduction

Cyclohexene is of great significant in modern industry, which can be applied as an intermediate for production of cyclohexanone, adipic acid, caprolactam, nylon 6, nylon 66 and so on [1,2]. Due to the safety, energy conservation, environmental friendly and might result in high carbon atom economy, it has been drawn much attention for the production of cyclohexene via selective hydrogenation of benzene [3]. However, the direct hydrogenation of benzene to cyclohexane is thermodynamically more favorable ($\Delta G = -98 \text{ kJ mol}^{-1}$, 25°C) than that obtained by selective hydrogenation to cyclohexene ($\Delta G = -23 \text{ kJ mol}^{-1}$, 25°C) [4]. Further, the double bond of cyclohexene is not stable under the

hydrogenation conditions, which could be easily continuously hydrogenated into cyclohexane [5]. Therefore, it has always been a goal to develop a catalytic system with relatively high activity and selectivity towards cyclohexene generation from the dynamics point of view [6–8].

Among all test catalysts, Ru is considered as the most promising candidate by demonstrating the high selectivity towards cyclohexene synthesis [9]. Surface modification is one of the most effective approaches to enhance the corresponding selectivity, from which promoters have been proven valid [10]. For instance, Cu [11], Co [12,13], Fe [14], Mn [15], Zn [16–20], La [21,22] and Ce [23] were reported to significantly improve the catalytic selectivity towards cyclohexene formation over Ru catalysts. Liu et al. [10] prepared Ru-Ce/SBA-15 catalyst via an impregnation method. They found that Ce existed as Ce^{3+} , which may transfer electrons from Ru and enhance the hydrophilicity of the catalyst surface, leading to the improvement of selectivity over Ru catalyst. In addition, Ru-M (M = Fe [24], Mn [24], Zn [24], La [25] and Ce [26]) catalysts were synthesized by Sun et al., from which Fe_3O_4 , Mn_3O_4 , ZnO , La_2O_3 and CeO_2 were observed, which could considerably increase the selectivity towards cyclohexene production over Ru catalyst.

On the other hand, in order to improve the selectivity of Ru catalyst towards cyclohexene generation, additives are generally used in the reaction system directly. Struijk et al. [27] thoroughly investigated ZnSO_4 , MnSO_4 , CrSO_4 , CoSO_4 , FeSO_4 , NiSO_4 and CdSO_4 as reaction additives, and deemed that these additives could not only increase the hydrophilicity of Ru surface, but also occupy parts of the active sites, which are not suitable for cyclohexene formation. Furthermore, Liu et al. [28] also showed that CdSO_4 and ZnSO_4 could be utilized as coadditives. It is suggested that CdSO_4 could retard the adsorption of cyclohexene, and ZnSO_4 was able to stabilize the formed cyclohexene and accelerate desorption of cyclohexene from Ru surface. This leads to the inhibition of further hydrogenation of cyclohexene to cyclohexane, thus increase the selectivity towards cyclohexene production.

It is well established that metal catalysts surrounded by metal oxides could effectively suppress the formation of coke and agglomeration of the active component [29,30]. Therefore, in this work, based on the research of promoters for partial hydrogenation of benzene over Ru catalyst, Ru catalyst surrounded by Mn_3O_4 was synthesized via a precipitation-reduction-gel method (denoted as $\text{Ru}@\text{Mn}_3\text{O}_4$). And the effect of ZnSO_4 , MnSO_4 and FeSO_4 as reaction additives was investigated on the selective hydrogenation of benzene towards cyclohexene.

2. Materials and Methods

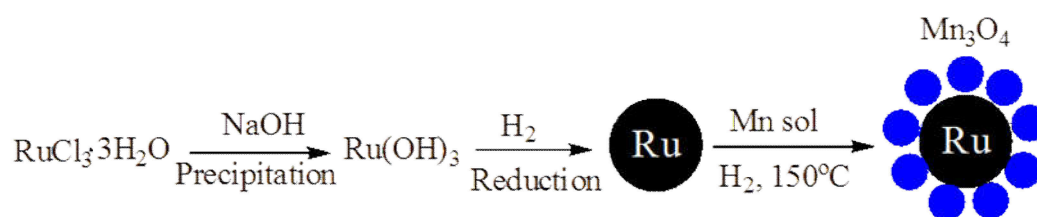
2.1. Chemicals

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was commercially obtained from Sino-Platinum Co. Ltd. (Kunming, China). $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, NaOH and benzene were delivered from Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). All chemicals were of analytical grade without further purification and distilled water was applied in all experiments.

2.2. Preparation of Catalysts

Monometallic Ru catalysts were prepared via the following procedure: 100 mL of 5 wt % NaOH aqueous solution was added in 100 mL of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ solution with concentration of 0.18 mol L^{-1} at 353 K with continuous stirring. After 15 min of stirring, the whole solution was poured in a 1000 mL Hastelloy autoclave (Weihai Chemical Machinery Co., Ltd. Weihai, China) under 5.0 MPa of H_2 and a stirring speed of 800 min^{-1} at 433 K for 3 h. Then the Ru catalyst was cooled down to room temperature, followed by washing with distilled water until neutral and vacuum-dried. Ru catalyst surrounded by Mn_3O_4 was synthesized by the following: certain amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.58 g of citric acid was added in 200 mL of distilled water, and the pH was adjusted to 6–7. Subsequently, the aqueous solution heated in water-bath of 333 K to become the Mn_3O_4 -gel. Then the obtained Ru catalyst as well as Mn_3O_4 -gel was added in the aforementioned Hastelloy autoclave under 5.0 MPa of H_2 and a stirring speed of 800 min^{-1} at 433 K for 5 h. After the cooling, washing and vacuum-drying,

the obtained material was denoted as Ru@Mn₃O₄(*x*), where *x* stands for the molar ratio of Mn to Ru. The preparation procedure of Ru@Mn₃O₄(*x*) catalysts is illustrated in Scheme 1.



Scheme 1. Preparation procedure of Ru@Mn₃O₄(*x*) catalysts.

2.3. Catalytic Experimental Procedure

All catalytic experiments were conducted in a 1000 mL GS-1 type Hastelloy autoclave. Of the Ru@Mn₃O₄ catalyst 1.8 g and 280 mL of 0.57 mol L⁻¹ ZnSO₄·7H₂O aqueous solution were added in the autoclave. Then the reactor was purified using N₂ for 4 times and followed by purification with H₂ for another 4 times. After the reactor was heated up to 423 K under 5.0 MPa of H₂ with a stirring speed of 800 min⁻¹, 140 cm³ benzene and adjusting the stirring speed to 1400 min⁻¹ to eliminate the mass transfer limitation. Subsequently, the liquid samples were taken periodically from the reactor every 5 min. All withdrawn samples were analyzed by gas chromatography from Hangzhou Kexiao Chemical Instrument and Equipment Co. Ltd. (Hangzhou, China) equipped with a flame ionization detector (FID). All reagents and products (e.g., benzene, cyclohexene and cyclohexane) were carefully calibrated, and correlation coefficient (*R*²) of all compounds is higher than 0.99. And the benzene conversion and selectivity towards cyclohexene were calculated with the obtained peak area with the area normalization method. To avoid the impact of Zn²⁺ on characterization results, catalysts after the reaction were filtered and washed until the filtrate become neutralization and no Zn²⁺ was detected. Then solid samples were dried in Ar flow at 373 K and stored in the ethanol for further characterization.

2.4. Procedure Catalysts Characterization

X-ray diffraction (XRD) patterns for the catalysts before and after catalytic reactions were recorded at room temperature using an X'Pert Pro instrument from PANalytical Company (Almelo, The Netherlands). The diffracted intensity of Cu-Kα radiation ($\lambda = 0.15418$ nm) was measured at the range of 2θ from 5° to 90°, with a step size of 0.03°. Textural properties were given by the Nova 1000e-Physisorption Analyzer from Quantachrome Company (Boynton Beach, FL, USA). All samples were pretreated at 523 K under the vacuum pressure for 2 h before the measurements and the isotherms were taken at 77 K. The specific surface area (*S*_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) model. Furthermore, elemental analysis was gained by X ray fluorescence (XRF) using a S4 Pioneer instrument from Bruker Company (Bruker AXS, Karlsruhe, Germany). In addition, the sample preserved in the ethanol was firstly dispersed with supersonic for 30 min, and then placed on a Cu net-board for TEM analysis using a JEOL JEM 2100 transmission electron microscope (TEM, Akishima, Tokyo, Japan), which combined with energy dispersive spectrometer (EDS) to identify the surface composition of the selected samples. Moreover, the valence state of Ru and Zn on the catalyst surface was explored by X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM instrument from UIVAC-PHI Company (Kangawa, Japan). Al Kα (*E*_b = 1486.6 eV) was selected as the source of radiation and vacuum degree was adjusted to be 6.7 × 10⁻⁸ Pa. The energy scale was calibrated and corrected for charging using the C1s (*E*_b = 284.8 eV) line as the binding energy reference.

3. Results and Discussions

3.1. Effect of Coated Mn_3O_4 Amount

XRD patterns of fresh $Ru@Mn_3O_4(x)$ catalyst with different content of Mn_3O_4 are illustrated in Figure 1a–c. Characteristic diffractions corresponding to metallic Ru with the hexagonal phase (PDF:01-070-0274) were observed over all measured samples, demonstrating that Ru existed mainly as the metallic state. Furthermore, when the molar ratio of Mn_3O_4 to Ru rose up to 0.46, the reflections related to Mn_3O_4 of tetragonal phase (PDF:00-001-1127 and PDF: 03-065-2776) started to be shown. This suggests that Ru was successfully coated by Mn_3O_4 . When the molar ratio of Mn_3O_4 to Ru was less than 0.46, no Mn corresponded reflection was observed. This might be mainly due to the fact that the surrounded Mn_3O_4 is lower than the detect limitation. Figure 1b shows the $Ru@Mn_3O_4(x)$ catalyst with different content of Mn_3O_4 after catalytic experiments. It can be seen that Ru still existed as the metallic state. On the other hand, as shown in Figure 1b, characteristic diffractions corresponding to metallic Ru with hexagonal phase could also be observed, suggesting that Ru still existed as metallic Ru. Notably, diffractions related to $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ (PDF:00-039-0689) and $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_{0.5}$ (PDF:00-044-0674) started to appear when the molar ratio of Mn to Ru reached 0.46 and 0.90, respectively. Additionally no Mn_3O_4 reflections could be seen. This is mainly attributed to Mn_3O_4 being able to react with $ZnSO_4$ under the reaction conditions to form $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_n$ ($n = 0.5$ or 3). It was also confirmed by Sun et al. [15,24] that Mn in Ru-Mn catalysts existed as Mn_3O_4 , which could react with $ZnSO_4$ to generate $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$.

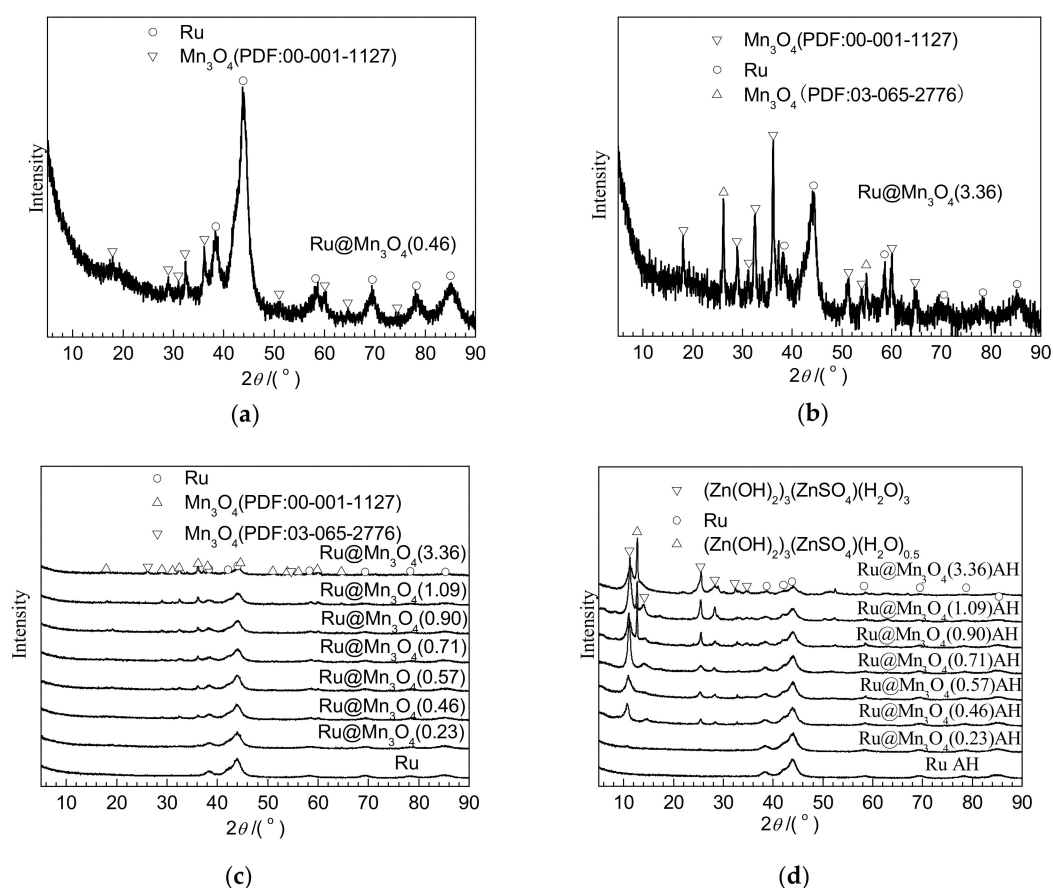


Figure 1. XRD patterns of $Ru@Mn_3O_4(x)$ before (a–c) and after (d) catalytic experiments. AH means after hydrogenation reactions.

Table 1 illustrates the textural properties and crystallite size of pure Ru as well as Ru@Mn₃O₄(*x*) before and after hydrogenation reactions. The crystallite size of fresh and spent monometallic Ru catalyst was quite comparable, i.e., 3.6 nm vs. 3.7 nm. This shows that the crystallite of Ru almost had no change during the reaction. Furthermore, the crystallite size of Ru@Mn₃O₄(*x*) was larger than that obtained over monometallic Ru no matter before and after hydrogenation reactions, suggesting that the coated Mn₃O₄ caused the enhancement of Ru crystallite size. On the other hand, all specific surface area, pore volume and pore diameter over the fresh catalysts tended to decrease with raising the amount of Mn₃O₄, implying that the surrounded Mn₃O₄ blocked part of the macropores and mesopores of Ru catalysts. More importantly, in comparison to that observed for fresh catalysts, there is a drastically decline on the specific surface area and the pore volume after the catalytic experiments. This suggests that more pores of Ru@Mn₃O₄ were blocked by the formed (Zn(OH)₂)₃(ZnSO₄)(H₂O)_{*n*} (*n* = 0.5 or 3) during the reaction.

Table 1. Texture properties and crystallite size of monometallic Ru as well as Ru@Mn₃O₄(*x*) before and after catalytic experiments.

Sample	BET Surface Area (cm ² /g) ¹	Pore Volume (cm ³ /g) ¹	Pore Diameter (nm) ¹	Ru Crystallite Size (nm) ²
Ru	59	0.18	10.63	3.6
Ru@Mn ₃ O ₄ (0.23)	57	0.20	13.74	3.9
Ru@Mn ₃ O ₄ (0.46)	41	0.11	10.98	4.1
Ru@Mn ₃ O ₄ (0.57)	52	0.15	11.35	4.8
Ru@Mn ₃ O ₄ (0.71)	47	0.17	15.79	4.4
Ru@Mn ₃ O ₄ (0.90)	54	0.15	11.20	4.6
Ru@Mn ₃ O ₄ (1.09)	39	0.10	10.20	4.7
Ru@Mn ₃ O ₄ (3.36)	27	0.07	9.48	4.6
Ru AH	56	0.16	10.44	3.7
Ru@Mn ₃ O ₄ (0.23) AH ³	56	0.15	11.03	4.2
Ru@Mn ₃ O ₄ (0.46) AH	41	0.11	10.98	4.5
Ru@Mn ₃ O ₄ (0.57) AH	33	0.13	15.79	4.6
Ru@Mn ₃ O ₄ (0.71) AH	30	0.13	16.92	4.8
Ru@Mn ₃ O ₄ (0.90) AH	29	0.11	15.34	4.7
Ru@Mn ₃ O ₄ (1.09) AH	26	0.08	12.93	4.2
Ru@Mn ₃ O ₄ (3.36) AH	14	0.03	8.72	4.7

¹ Measured by a N₂ physisorption instrument. ² Measured by a XRD instrument. ³ AH means after hydrogenation reactions.

Composition of pure Ru and Ru@Mn₃O₄(*x*) catalysts after catalytic experiments is listed in Table 2. As can be seen, by increasing the amount of coated Mn₃O₄, very few Mn species was kept on the Ru surface after the hydrogenation reaction. Unlike what observed for Mn species, an obvious raise of Zn and S content was noticed with enhancing the coated Mn₃O₄ content. This implies that Mn₃O₄ could react with ZnSO₄, generating (Zn(OH)₂)₃(ZnSO₄)(H₂O)_{*n*} (*n* = 0.5 or 3), MnSO₄ and Mn₂(SO₄)₃ (e.g., Equations (1) and (2)). Among all formed compounds, MnSO₄ and Mn₂(SO₄)₃ were mostly dissolved in the slurry, where (Zn(OH)₂)₃(ZnSO₄)(H₂O)_{*n*} (*n* = 0.5 or 3) was adsorbed on the Ru surface. Therefore, more (Zn(OH)₂)₃(ZnSO₄)(H₂O)_{*n*} (*n* = 0.5 or 3) could be produced by increasing the amount of coated Mn₃O₄.

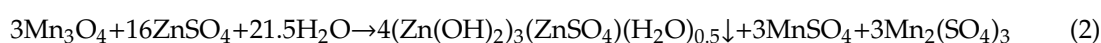
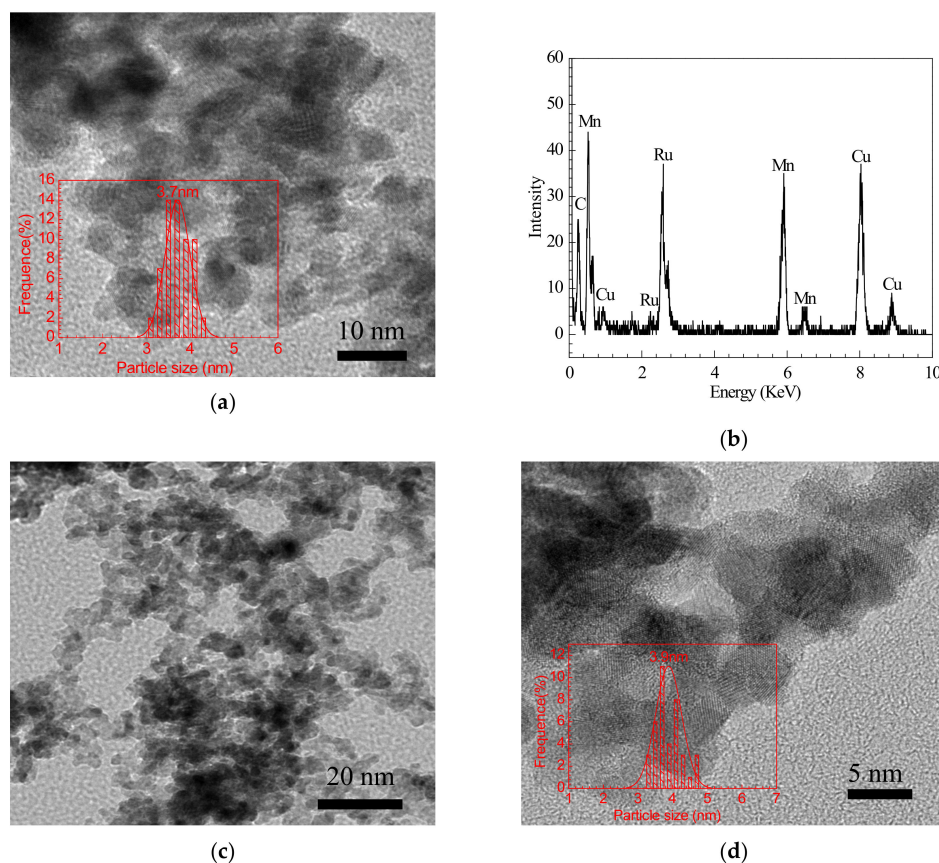


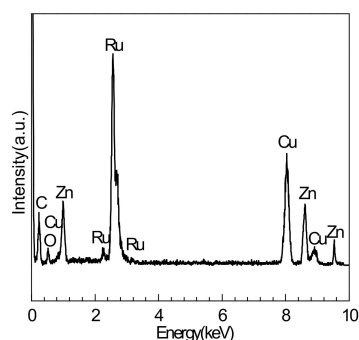
Table 2. Composition of monometallic Ru as well as Ru@Mn₃O₄(x) after catalytic experiments.

Catalyst	n(Mn)/n(Ru) (mol/mol) ¹	n(Zn)/n(Ru) (mol/mol) ¹	n(S)/n(Ru) (mol/mol) ¹
Ru AH	0	0.0313	0.0026
Ru@ Mn ₃ O ₄ (0.23) AH ²	0.0207	0.2010	0.0149
Ru@ Mn ₃ O ₄ (0.46) AH	0.0206	0.5085	0.0619
Ru@ Mn ₃ O ₄ (0.57) AH	0.0213	0.8369	0.1173
Ru@ Mn ₃ O ₄ (0.71) AH	0.0203	1.1733	0.1844
Ru@ Mn ₃ O ₄ (0.90) AH	0.0215	1.3726	0.2159
Ru@ Mn ₃ O ₄ (1.09) AH	0.0213	2.1539	0.3410
Ru@ Mn ₃ O ₄ (3.36) AH	0.0306	4.9727	0.9117

¹ Measured by an X ray fluorescence (XRF) instrument. ² AH means after hydrogenation reactions.

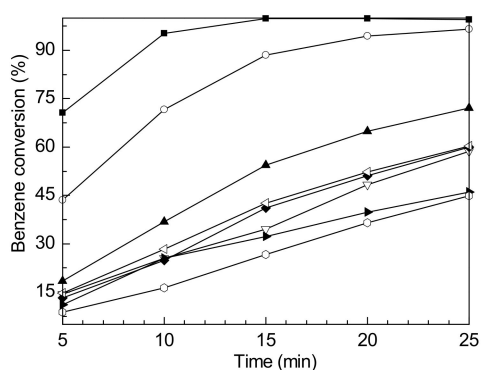
High-resolution TEM (HRTEM) and particle size distribution of fresh Ru@Mn₃O₄(0.46) are shown in Figure 2a. It can be observed that fresh Ru@Mn₃O₄(0.46) particles were in a circular or elliptical shape, and particle size of the sample was around 3.7 nm. Figure 2b displays the EDS spectrum of fresh Ru@Mn₃O₄(0.46). Besides the C and Cu from contaminated CO₂ and Cu net-board, Ru and Mn were the main elements on the catalyst surface. This again proves that Mn₃O₄ is successfully coated on the Ru surface. As can be seen from Figure 2c,d, the spent Ru@Mn₃O₄(0.46) still displayed circular or elliptical shape, and its particle size was approximately 3.9 nm. This indicates that the particle shape remained the same, which is in a good agreement with that obtained from XRD results. Furthermore, EDS spectrum of spent Ru@Mn₃O₄(0.46) was shown in Figure 3e. In comparison to that observed over fresh Ru@Mn₃O₄(0.46) (Figure 3b), reflections of Zn element was demonstrated, while Mn can no longer be seen. This indicates that Mn₃O₄ could react with ZnSO₄, generating (Zn(OH)₂)₃(ZnSO₄)(H₂O)_x (x = 3 or 0.5), which is in a good agreement with XRD results.

**Figure 2.** Cont.

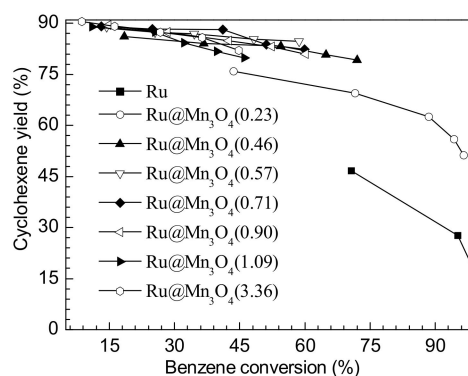


(e)

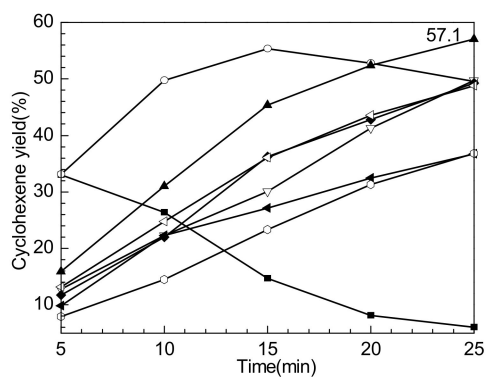
Figure 2. HRTEM (a), particle size distribution (insert image) and EDS (b) of fresh Ru@Mn₃O₄(0.46) as well as TEM (c), HRTEM (d), particle size distribution (insert image) and EDS (e) of spent Ru@Mn₃O₄(0.46).



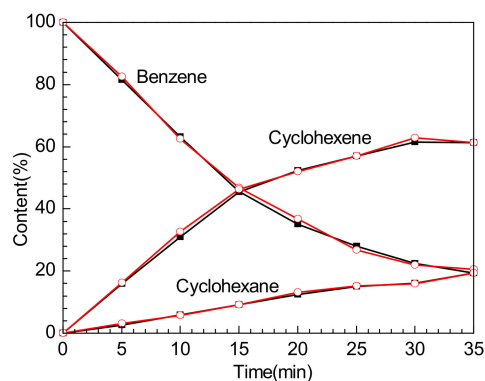
(a)



(b)



(c)



(d)

Figure 3. Catalytic activity towards cyclohexene formation from selective hydrogenation of benzene over Ru@Mn₃O₄(*x*) catalyst in the presence of ZnSO₄ with the different molar ratio of Mn to Ru as well as the kinetic curve over Ru@Mn₃O₄(0.46) ($m_{\text{cat}} = 1.8 \text{ g}$, $c_{\text{ZnSO}_4} = 0.57 \text{ mol L}^{-1}$, $v_{\text{H}_2\text{O}} = 280 \text{ mL}$, $v_{\text{benzene}} = 140 \text{ mL}$, $T = 423 \text{ K}$, $p_{\text{H}_2} = 5.0 \text{ MPa}$). (a): Benzene conversion; (b): cyclohexene selectivity; (c): cyclohexene yield and (d): kinetic curve over Ru@Mn₃O₄(0.46).

Catalytic activity towards cyclohexene formation from selective hydrogenation of benzene over the Ru@Mn₃O₄(*x*) catalyst is given in Figure 3a–c. It is obvious that the coated Mn₃O₄ significantly improved the selectivity towards cyclohexene formation and diminished the activity towards benzene conversion. When the molar ratio of Mn to Ru was 0.46, 72.0% of benzene conversion, 79.2% of

cyclohexene selectivity and 57.0% of yield was achieved within 25 min of reaction time. From the industrial aspect, due to the comparable boiling point, the separation among benzene, cyclohexane and cyclohexene cannot be easily done via a simple distillation procedure. Dimethylacetamide is commonly used as an extractor for the separating purpose [31]. Therefore, selectivity towards cyclohexene production is highly desired in industry to simplify the separation procedure, of which 80% are normally required [9]. Currently, 40% of benzene conversion, 80% of cyclohexene selectivity and 32% of cyclohexene yield meet the basic requirement of cyclohexene production from selective hydrogenation of benzene over a Ru-Zn catalyst in real industry [31]. Thus, Ru@Mn₃O₄(0.46) is quite promising as an alternative candidate.

Combined with the characterization results and that reported in the literatures, it is deemed that (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n (*n* = 0.5 or 3) plays a key role on the formation of cyclohexene. This can be rationalized in terms of the following reasons: (1) A stable complex could be formed between (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n and cyclohexene, retarding the further hydrogenation of cyclohexene to cyclohexane. Sun et al. [32] reported that Δ*G* of −618.7 kJ mol^{−1} and −1075.6 kJ mol^{−1} was gained for the complex generated from Zn²⁺ with one and two cyclohexene molecules, respectively. (2) There are several hydroxyl and crystal water in (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n, generating a stagnant water layer on the catalyst surface. Since the solubility of cyclohexene is lower than that of benzene, it favors desorption of the generated cyclohexene from the catalyst surface through the stagnant water layer, hence suppressing the further hydrogenation of cyclohexene [33]. (3) Part of pores of Ru particles could be blocked by the formed (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n, resulting in that the hydrogenation of benzene mainly takes place on the surface of catalyst. This further leads to the enhancement of the selectivity towards cyclohexene due to its easy desorption from Ru surface. It was stated by Struijk et al. [33] that cyclohexene generation only occurred on the outer-surface of Ru. (4) (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n was preferentially adsorbed on the most active sites of Ru [27], leaving the rest active sites with weaker ability for adsorption of benzene and cyclohexene. This would drastically improve the selectivity towards cyclohexene formation, while declining the activity towards benzene conversion. It is in a good agreement with what is observed in this work (Figure 3a–c). (5) There is a strong interaction between Ru and Zn²⁺, which will be further discussed in Section 3.2.

Figure 3d displays the kinetic curve of cyclohexene formation from hydrogenation of benzene over Ru@Mn₃O₄(0.46). Of the cyclohexene yield 61.4% was achieved within 30 min of reaction time, which is among the highest yields of cyclohexene ever reported [8,10]. More importantly, it still remained at 61.3% after 35 min of catalytic experiment, describing that (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n (*n* = 0.5 or 3) could significantly inhibit the further hydrogenation of cyclohexene towards cyclohexane generation. On the other hand, to disprove the homogeneous catalytic effect of Mn salts, a preformed Ru@Mn₃O₄(0.46)-ZnSO₄ catalyst was prepared by adding Ru@Mn₃O₄(0.46) in the 0.58 mol/L aqueous solution of ZnSO₄, followed by a treatment at 433 K under 5 MPa of H₂ for 30 min. Then the filtered solid was washed and further tested for partial hydrogenation of benzene (red line in Figure 3d). Identical results was achieved over Ru@Mn₃O₄(0.46)-ZnSO₄ in comparison to that obtained over Ru@Mn₃O₄(0.46), suggesting no homogeneous catalytic effect of Mn salts in this work. Since (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n is generated via the reaction between the promoter (e.g., Mn₃O₄) and the additive (e.g., ZnSO₄), it is deemed that the additives are also of great importance for improving the selectivity towards cyclohexene synthesis. Therefore, the effect of additives on selective hydrogenation of benzene over Ru@Mn₃O₄(0.46) will be thoroughly investigated.

3.2. Effect of Additives

Figure 4 demonstrates the XRD patterns of Ru@Mn₃O₄(0.46) with ZnSO₄, MnSO₄ and FeSO₄ as additives after catalytic experiments. As expected, characteristic diffractions corresponding to metallic Ru were observed over all analyzed samples, indicating that Ru still existed as metallic state with the addition of ZnSO₄, MnSO₄ and FeSO₄ after the hydrogenation reaction. Besides, reflections related to (Zn(OH)₂)₃(ZnSO₄)(H₂O)_n (*n* = 0.5 or 3) were detected by adding 0.28 mol L^{−1}

and 0.57 mol L⁻¹ of ZnSO₄, respectively. This suggests that varying concentration of added ZnSO₄ causes different content of crystal water. Furthermore, diffractions of Mn₃O₄ (PDF:00-001-1127) and MnSO₄·H₂O (PDF:00-014-0166) of tetragonal phase were observed when MnSO₄ was applied as an additive, implying that MnSO₄·H₂O can hardly react with Mn₃O₄. Additionally, part of the excessive amount of MnSO₄·H₂O could be adsorbed on the Ru surface.

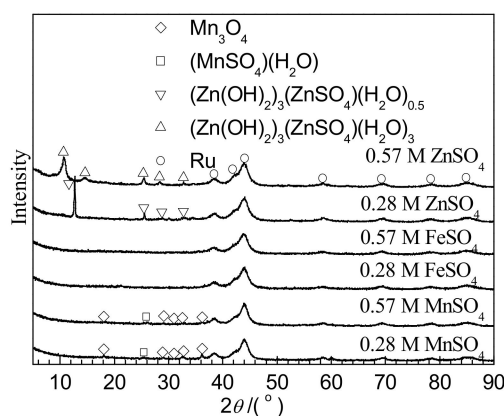


Figure 4. XRD patterns of spent Ru@Mn₃O₄(0.46) with 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives, respectively.

XPS profiles of spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives are demonstrated in Figure 5. As can be observed, three peaks related to binding energy (BE) of Mn2p_{3/2} were observed at 641.7, 643.4 and 646.2 eV, which are attributed to Mn²⁺, Mn³⁺ and Mn⁴⁺, respectively [34]. Additionally, the peak area obtained over Mn²⁺ and Mn³⁺ was much larger than that given by Mn⁴⁺, indicating that Mn mainly existed as Mn²⁺ and Mn³⁺ state. Moreover, BE of Zn2p_{3/2} over spent Ru@Mn₃O₄(0.46) catalyst was observed to be 1021.8 eV, which is extremely close to that reported for (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ (e.g., 1021.9 eV) [17]. These are consistent with that obtained from XRD results. Furthermore, BE of Fe2p_{3/2} over the spent Ru@Mn₃O₄(0.46) catalyst was shown at 710.4 and 712.6 eV, relating to Fe²⁺ and Fe³⁺, respectively. The small peak at 718.1 eV was attributed to the satellite reflection of Fe²⁺ [35]. This indicates that Fe on the surface of the spent Ru@Mn₃O₄(0.46) catalyst existed as Fe²⁺ and Fe³⁺. On the other hand, the BE of Ru2p_{3/2} over spent Ru@Mn₃O₄(0.46) without any additives is close to that reported over metallic Ru (461.1 eV) [36]. This implies that electrons were hardly transferred between Ru and Mn₃O₄. In addition, the BE of Ru2p_{3/2} over spent Ru@Mn₃O₄(0.46) with MnSO₄ as an additive is the same as that achieved over spent Ru@Mn₃O₄(0.46) without any additives, indicating that no electron transfer occurred between Mn and Ru. However, when ZnSO₄ and FeSO₄ was applied, the BE of Ru2p_{3/2} over spent Ru@Mn₃O₄(0.46) was raised to 462.1 and 462.5 eV, respectively. This suggests that a number of electrons were transferred from Ru to Zn or Fe, generating the Ru^{δ+} species. Additionally, more electrons were transferred from Ru to Fe than that transferred from Ru to Zn.

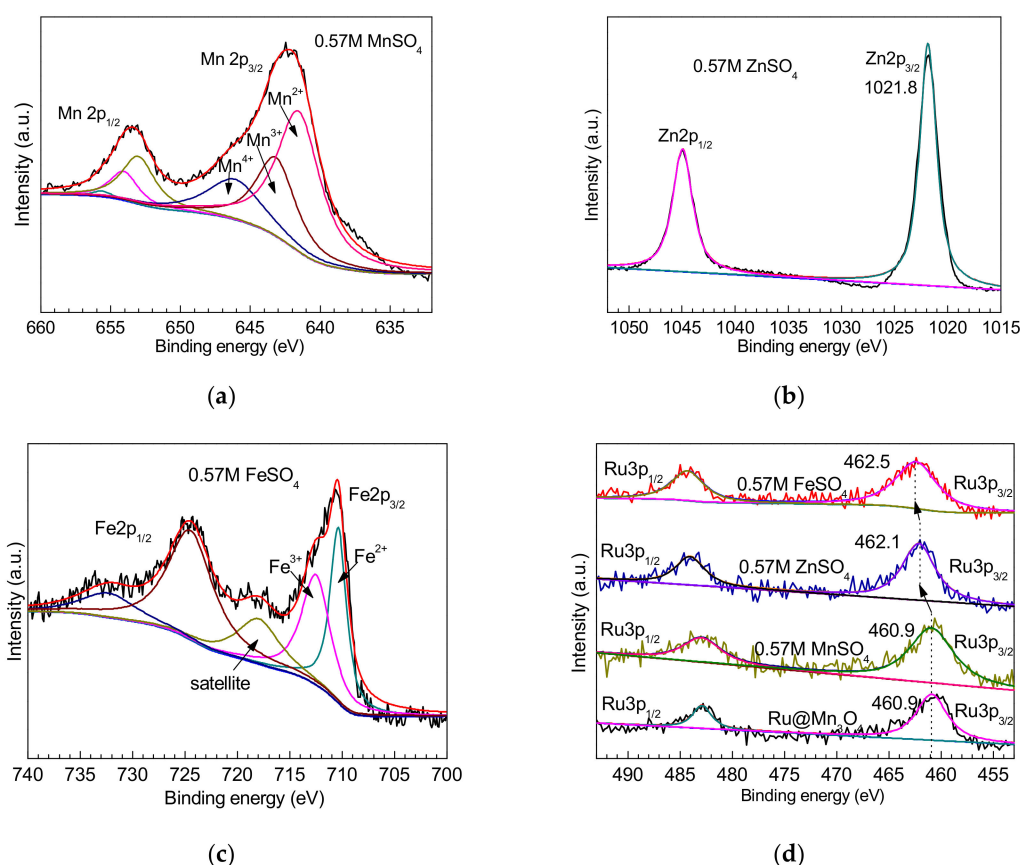


Figure 5. XPS profiles of spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives, respectively. (a): Mn 2p of spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ MnSO₄; (b): Zn 2p of spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ ZnSO₄; (c): Fe 2p of spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ FeSO₄ and (d) Ru 3p of the fresh Ru@Mn₃O₄(0.46) catalyst and the spent Ru@Mn₃O₄(0.46) catalyst with 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives.

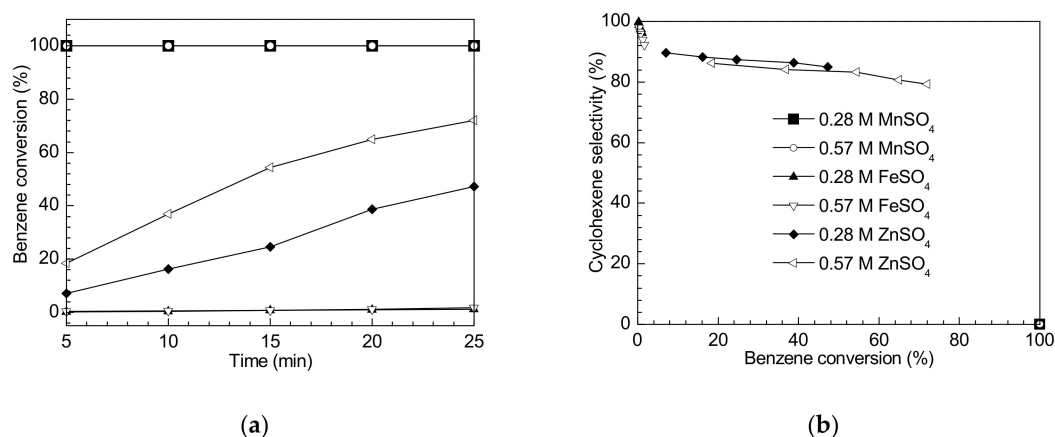
Composition of spent Ru@Mn₃O₄(0.46) with applying 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives is listed in Table 3. It can be seen that, by adding MnSO₄, Ru, Mn and S were detected on the surface of spent Ru@Mn₃O₄(0.46), demonstrating the presence of Ru, Mn₃O₄ and MnSO₄. Notably, molar ratio of Mn/Ru and S/Ru was quite comparable, suggesting that a similar content of Mn₃O₄ and MnSO₄ were preserved on the Ru surface remained the same despite the different concentration of applied MnSO₄. It is worth mentioning that the molar ratio of Mn to Ru drastically dropped when FeSO₄ was added in comparison to that obtained with addition of MnSO₄, suggesting that Mn₃O₄ could react with FeSO₄. Meanwhile, a similar trend was observed when different concentration of FeSO₄ was utilized, where close molar ratio of Mn/Ru, Fe/Ru and S/Ru was obtained. This shows that the amount of generated Fe compounds via the reaction between Mn₃O₄ and FeSO₄ was comparable. Similarly, by addition of ZnSO₄, the molar ratio of Mn to Ru drastically decreased in comparison to that obtained with addition of MnSO₄. This is mainly due to the fact that the added ZnSO₄ could react with Mn₃O₄ to generate (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃. Interestingly, when 0.57 mol L⁻¹ of ZnSO₄ was applied, the molar ratio of Zn/Ru and S/Ru was 0.2010 and 0.0149, respectively. This is obvious lower than the molar ratio of Zn/Ru and S/Ru by adding 0.28 mol L⁻¹ of ZnSO₄ (0.4997 and 0.0481, respectively). This might be attributed to the hydrolysis of ZnSO₄, from which the generated acid could react with (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃, and thus reduced that content of adsorbed (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ on the Ru surface.

Table 3. Composition of spent Ru@Mn₃O₄(0.46) with applying 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives.

Additive	$n(\text{Mn})/n(\text{Ru})$ (mol/mol) ¹	$n(\text{Zn})/n(\text{Ru})$ (mol/mol) ¹	$n(\text{Fe})/n(\text{Ru})$ (mol/mol) ¹	$n(\text{S})/n(\text{Ru})$ (mol/mol) ¹
0.28 M MnSO ₄	0.5006	-	-	0.0503
0.57 M MnSO ₄	0.4728	-	-	0.0507
0.28 M FeSO ₄	0.0195	-	0.4642	0.0374
0.57 M FeSO ₄	0.0172	-	0.4681	0.0321
0.28 M ZnSO ₄	0.0222	0.4997	-	0.0481
0.57 M ZnSO ₄	0.0207	0.2010	-	0.0149

¹ Measured by an XRF instrument.

Figure 6 shows the catalytic activity towards benzene conversion and cyclohexene selectivity over the Ru@Mn₃O₄(0.46) catalyst with adding ZnSO₄, MnSO₄ and FeSO₄ with a concentration of 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ as additives. Interestingly, complete conversion of benzene was observed within 5 min when MnSO₄ (both 0.28 and 0.57 mol L⁻¹) was applied, and no cyclohexene was obtained. This can be rationalized in terms that no electron was transferred between Ru and Mn species. Besides, Ru@Mn₃O₄(0.46) was also evaluated in the absence of ZnSO₄, over which complete benzene conversion and 100% of cyclohexane yield was obtained. This further implies that no electron was transferred between Ru and Mn species. On contrary, only 1.2% and 1.5% of benzene conversion as well as 96.2% and 92.2% of cyclohexene selectivity was gained with addition of 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ FeSO₄, respectively. On the other hand, when ZnSO₄ was applied as an additive, especially with the concentration of 0.57 mol L⁻¹, considerably high activity towards benzene conversion (e.g., 72.0%) and selectivity towards cyclohexene (e.g., 79.2%) was achieved. Additionally, 43.7% of benzene conversion and 84.9% of cyclohexene selectivity were obtained over Ru@Mn₃O₄(0.46) by using ZnSO₄ of 0.28 mol L⁻¹ as an additive, which was still superior to that gained by using MnSO₄ and FeSO₄.

**Figure 6.** Catalytic activity towards benzene conversion and cyclohexene selectivity over Ru@Mn₃O₄(0.46) catalyst with adding 0.28 mol L⁻¹ as well as 0.57 mol L⁻¹ of ZnSO₄, MnSO₄ and FeSO₄ as additives ($m_{\text{cat}} = 1.8$ g, $v_{\text{H}_2\text{O}} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $p_{\text{H}_2} = 5.0$ MPa). (a): Benzene conversion and (b): cyclohexene selectivity.

Based on the above discussions, it was confirmed that more electrons were transferred from Ru to Fe than that transferred from Ru to Zn. Therefore, it is concluded that the loss of electrons from Ru plays a key role on the enhancement of selectivity towards cyclohexene formation as well as the decline of activity towards benzene conversion. It is also confirmed that Ru^{δ+} species is crucial in the production of cyclohexene from selective hydrogenation of benzene over Ru-based catalysts [2,6,37]. This can be attributed to the followed two reasons: (1) Less electrons from *d*-orbital of Ru^{δ+} species can be used to active the π -orbital of benzene, leading to that benzene could hardly be directly hydrogenated to

cyclohexane [22]. This favors the formation of cyclohexene; (2) the adsorption enthalpy of cyclohexene over $\text{Ru}^{\delta+}$ is much lower than that over Ru^0 , accelerating the desorption of cyclohexene and thus improves the selectivity towards cyclohexene synthesis. Meanwhile, the adsorption enthalpy of benzene over $\text{Ru}^{\delta+}$ is also lower than that over Ru^0 , resulting in the decrease of catalytic activity towards benzene conversion [37]. Hence, the highest selectivity towards cyclohexene formation and the lowest activity towards benzene conversion was achieved over $\text{Ru@Mn}_3\text{O}_4(0.46)$ catalyst when FeSO_4 was added, since the most $\text{Ru}^{\delta+}$ species were generated. In addition, with increasing the amount of adsorbed $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_n$ ($n = 0.5$ or 3), more electrons from Ru could be transferred to Zn^{2+} . This leads to the increasement of cyclohexene selectivity and decline of benzene conversion. Therefore, due to the lower molar ratio of Zn/Ru by using 0.57 mol L^{-1} ZnSO_4 than that obtained by applying 0.28 mol L^{-1} of ZnSO_4 , higher catalytic activity towards benzene conversion and lower selectivity to cyclohexene was observed when more ZnSO_4 was introduced.

4. Conclusions

$\text{Ru@Mn}_3\text{O}_4$ with different Mn_3O_4 content was synthesized via a precipitation-reduction-gel method. It was found that 72.0% of benzene conversion and 79.2% of cyclohexene selectivity was achieved after 25 min of reaction time over $\text{Ru@Mn}_3\text{O}_4$ with molar ratio of Mn/Ru being 0.46. This can be rationalized in terms of the formed $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ on Ru surface from the reaction between Mn_3O_4 and the added ZnSO_4 . Furthermore, Fe^{2+} and Fe^{3+} compounds could be generated and adsorbed on the surface of $\text{Ru@Mn}_3\text{O}_4$ when FeSO_4 is applied as a reaction additive. The most electrons were transferred from Ru to Fe, resulting in that lowest benzene conversion of 1.5% and the highest cyclohexene selectivity of 92.2% after 25 min. On the other hand, by utilizing MnSO_4 as an additive, no electrons transfer was observed between Ru and Mn, which led to the complete hydrogenation of benzene towards cyclohexane within 5 min. In comparison, a moderate amount of electrons were transferred from Ru to Zn^{2+} in $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ when ZnSO_4 was used as a reaction additive, and the highest cyclohexene yield of 57.0% was obtained within 25 min. The effect of reaction additives can be mainly attributed to that the corresponding metal ions adsorbed on the Ru surface and transfer a few electrons from Ru. This leads to the generation of $\text{Ru}^{\delta+}$ species and thus improves the selectivity towards cyclohexene.

Author Contributions: X.L. was responsible for conducting the experiments and data analysis. Z.C. and H.S. were responsible for designing the experiments and manuscript preparation. Z.P. was responsible for making figures. L.C. and Z.L. were responsible for all the chemical purchase and characterization of the samples. All authors have read and agreed to the published version of the manuscript.

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References

1. Yan, X.H.; Zhang, Q.; Zhu, M.Q.; Wang, Z.B. Selective hydrogenation of benzene to cyclohexene over Ru-Zn/ZrO₂ catalysts prepared by a two step impregnation method. *J. Mol. Catal. A Chem.* **2016**, *413*, 85–93. [[CrossRef](#)]
2. Gonçalves, A.H.A.; Soares, J.C.S.; Araújo, L.R.R.; Zotin, F.M.Z.; Mendes, F.M.T.; Gaspar, A.B. Surface investigation by X-ray photoelectron spectroscopy of Ru-Zn catalysts for the partial hydrogenation of benzene. *Mol. Catal.* **2020**, *483*, 110710. [[CrossRef](#)]

3. Sun, H.J.; Chen, Z.H.; Li, C.G.; Chen, L.X.; Peng, Z.K.; Liu, Z.Y.; Liu, S.C. Selective Hydrogenation of Benzene to Cyclohexene over Ru-Zn Catalysts: Mechanism Investigation on NaOH as a Reaction Additive. *Catalysts* **2018**, *8*, 104. [[CrossRef](#)]
4. Sun, H.J.; Chen, Z.H.; Li, C.G.; Chen, L.X.; Li, Y.; Peng, Z.K.; Liu, Z.Y.; Liu, S.C. Selective Hydrogenation of Benzene to Cyclohexene over Monometallic Ru Catalysts: Investigation of ZnO and ZnSO₄ as Reaction Additives as Well as Particle Size Effect. *Catalysts* **2018**, *8*, 172. [[CrossRef](#)]
5. Sun, H.J.; Chen, Z.H.; Chen, L.X.; Li, H.J.; Peng, Z.K.; Liu, Z.Y.; Liu, S.C. Selective Hydrogenation of Benzene to Cyclohexene over Ru-Zn Catalysts: Investigations on the Effect of Zn Content and ZrO₂ as the Support and Dispersant. *Catalysts* **2018**, *8*, 513. [[CrossRef](#)]
6. Zhou, G.B.; Dou, R.F.; Bi, H.Z.; Xie, S.H.; Pei, Y.; Fan, K.N.; Qiao, M.H.; Sun, B.; Zong, B.N. Ru nanoparticles on rutile/anatase junction of P25 TiO₂: Controlled deposition and synergy in partial hydrogenation of benzene to cyclohexene. *J. Catal.* **2015**, *332*, 119–126. [[CrossRef](#)]
7. Peng, Z.K.; Liu, X.; Lin, H.N.; Wang, Z.; Li, Z.J.; Li, B.J.; Liu, Z.Y.; Liu, S.C. Surface engineering on a nanocatalyst: Basic zinc salt nanoclusters improve catalytic performances of Ru nanoparticles. *J. Mater. Chem. A* **2016**, *4*, 17694–17703. [[CrossRef](#)]
8. Zhou, G.B.; Pei, Y.; Jiang, Z.; Fan, K.N.; Qiao, M.H.; Sun, B.; Zong, B.N. Doping effects of B in ZrO₂ on structural and catalytic properties of Ru/B-ZrO₂ catalysts for benzene partial hydrogenation. *J. Catal.* **2014**, *311*, 393–403. [[CrossRef](#)]
9. Sun, H.J.; Guo, W.; Zhou, X.L.; Chen, Z.H.; Liu, Z.Y.; Liu, S.C. Process in Ru-based Amorphous Alloy Catalysts for Benzene Selective Hydrogenation to Cyclohexene. *Chin. J. Catal.* **2011**, *32*, 1–16. [[CrossRef](#)]
10. Liu, J.L.; Zhu, L.J.; Pei, Y.; Zhuang, J.H.; Li, H.; Li, H.X.; Qiao, M.H.; Fan, K.N. Ce-promoted Ru/SBA-15 catalysts prepared by a “two solvent” impregnation method for selective hydrogenation of benzene to cyclohexene. *Appl. Catal. A Gen.* **2009**, *353*, 282–287. [[CrossRef](#)]
11. Liu, H.Z.; Liang, S.G.; Wang, W.T.; Jiang, T.; Han, B.X. The partial hydrogenation of benzene to cyclohexene over Ru-Cu catalyst supported on ZnO. *J. Mol. Catal. A Chem.* **2011**, *341*, 35–41. [[CrossRef](#)]
12. Fan, G.Y.; Jiang, W.D.; Wang, J.B.; Li, R.X.; Chen, H.; Li, X.J. Selective hydrogenation of benzene to cyclohexene over RuCoB/γ-Al₂O₃ without additive. *Catal. Commun.* **2008**, *10*, 98–102. [[CrossRef](#)]
13. Sun, H.J.; Li, S.H.; Zhang, Y.X.; Jiang, H.B.; Qu, L.L.; Liu, Z.Y. Selective hydrogenation of benzene to cyclohexene in continuous reaction device with two reaction reactors in serie over Ru-Co-B/ZrO₂ catalysts. *Chin. J. Catal.* **2013**, *34*, 1482–1488. [[CrossRef](#)]
14. Sun, H.J.; Li, S.H.; Tian, X.Y.; Zhang, Y.X.; Jiang, H.B.; Liu, S.C.; Liu, Z.Y. Selective hydrogenation of benzene to cyclohexene over Ru catalyst modified by the promoter Fe and the reaction modifiers. *J. Mol. Catal. (China)* **2013**, *27*, 362–370.
15. Sun, H.J.; Jiang, H.B.; Li, S.H.; Wang, H.X.; Pan, Y.J.; Dong, Y.Y.; Liu, S.C.; Liu, Z.Y. Selective hydrogenation of benzene to cyclohexene over nanocomposite Ru-Mn/ZrO₂ catalyst. *Chin. J. Catal.* **2013**, *34*, 684–694. [[CrossRef](#)]
16. Wang, Z.B.; Zhang, Q.; Lu, X.F.; Chen, S.J.; Liu, C.J. Ru-Zn catalysts for selective hydrogenation of benzene using coprecipitation in low alkalinity. *Chin. J. Catal.* **2015**, *36*, 400–407. [[CrossRef](#)]
17. Sun, H.J.; Wang, H.X.; Jiang, H.B.; Li, S.H.; Liu, S.C.; Liu, Z.Y.; Yuan, X.M.; Yang, K.J. Effect of (Zn(OH)₂)₃(ZnSO₄)(H₂O)₅ on the performance of Ru-Zn catalyst for benzene selective hydrogenation to cyclohexene. *Appl. Catal. A* **2013**, *450*, 160–168. [[CrossRef](#)]
18. Sun, H.J.; Jiang, H.B.; Dong, Y.Y.; Wang, H.X.; Pan, Y.J.; Liu, S.C.; Tang, M.S.; Liu, Z.Y. Effect of alcohols as additives on the performance of a nano-sized Ru-Zn (2.8%) catalyst for selective hydrogenation of benzene to cyclohexene. *Chem. Eng. J.* **2013**, *218*, 415–424. [[CrossRef](#)]
19. Sun, H.J.; Chen, L.X.; Huang, Z.X.; Liu, S.C.; Liu, Z.Y. Particle Size Effect of Ru-Zn Catalysts on Selective Hydrogenation of Benzene to Cyclohexene. *Chem. J. Chin. U.* **2015**, *36*, 1969–1976.
20. Sun, H.J.; Chen, J.J.; Huang, Z.X.; Liu, Z.Y.; Liu, S.C. Selective hydrogenation of benzene to cyclohexene over the nano-sized Ru-Zn catalyst modified by Rrabic gum. *Chin. J. Inorg. Chem.* **2016**, *32*, 202–210.
21. Liao, H.G.; Ouyang, D.H.; Zhang, J.; Xiao, Y.J.; Liu, P.L.; Hao, F.; You, K.Y.; Luo, H.A. Benzene hydrogenation over oxide-modified MCM-41 supported ruthenium-lanthanum catalyst: The influence of zirconia crystal form and surface hydrophilicity. *Chem. Eng. J.* **2014**, *243*, 207–216. [[CrossRef](#)]

22. Sun, H.J.; Li, Y.Y.; Li, S.H.; Zhang, Y.X.; Liu, S.C.; Liu, Z.Y.; Ren, B.Z. ZnSO₄ and La₂O₃ as Co-Modifier of the Monoclinic Ru Catalyst for Selective Hydrogenation of Benzene to Cyclohexene. *Acta. Phys. Chim. Sin.* **2014**, *30*, 1332–1340.
23. Sun, H.J.; Chen, L.X.; Li, S.H.; Jiang, H.B.; Zhang, Y.X.; Ren, B.Z.; Liu, Z.Y.; Liu, S.C. Selective hydrogenation of benzene to cyclohexene over monometallic ruthenium catalysts in the presence of CeO₂ and ZnSO₄ as co-modifiers. *J. Rare Earths* **2013**, *31*, 1023–1028. [[CrossRef](#)]
24. Sun, H.J.; Pan, Y.J.; Jiang, H.B.; Li, S.H.; Zhang, Y.X.; Liu, S.C.; Liu, Z.Y. Effect of transition metals (Cr, Mn, Fe, Co, Ni, Cu and Zn) on the hydrogenation properties of benzene over Ru-based catalyst. *Appl. Catal. A Gen.* **2013**, *464–465*, 1–9. [[CrossRef](#)]
25. Sun, H.J.; Dong, Y.Y.; Li, S.H.; Jiang, H.B.; Zhang, Y.X.; Liu, Z.Y.; Liu, S.C. The role of La in improving the selectivity to cyclohexene of Ru catalyst for hydrogenation of benzene. *J. Mol. Catal. A Chem.* **2013**, *368–369*, 119–124. [[CrossRef](#)]
26. Sun, H.J.; Pan, Y.J.; Li, S.H.; Zhang, Y.X.; Dong, Y.Y.; Liu, S.C.; Liu, Z.Y. Selective hydrogenation of benzene to cyclohexene over Ce-promoted Ru catalysts. *J. Energy Chem.* **2013**, *22*, 710–716. [[CrossRef](#)]
27. Struijk, J.; Moene, R.; Kamp, T.V.D.; Scholten, J.J.F. Partial liquid phase hydrogenation of benzene to cyclohexene over ruthenium catalysts in the presence of an aqueous salt solution II. Influence of various salts on the performance of the catalyst. *Appl. Catal. A Gen.* **1992**, *89*, 77–102. [[CrossRef](#)]
28. Liu, J.L.; Zhu, Y.; Liu, J.; Pei, Y.; Li, Z.H.; Li, H.; Li, H.X.; Qiao, M.H.; Fan, K.N. Discrimination of the roles of CdSO₄ and ZnSO₄ in liquid phase hydrogenation of benzene to cyclohexene. *J. Catal.* **2009**, *268*, 100–105. [[CrossRef](#)]
29. Yi, H.; Du, H.Y.; Hu, Y.L.; Yan, H.; Jiang, H.L.; Lu, J.L. Precisely controlled porous alumina overcoating on Pd catalyst by atomic layer deposition: Enhanced selectivity and durability in hydrogenation of 1,3-Butadiene. *ACS Catal.* **2015**, *5*, 2735–2739. [[CrossRef](#)]
30. Wang, C.L.; Wang, H.W.; Yao, Q.; Yan, H.; Li, J.J.; Lu, J.L. Precisely applying TiO₂ overcoat on supported Au catalysts using atomic layer deposition for understanding the reaction mechanism and improved activity in CO oxidation. *J. Phys. Chem. C* **2016**, *120*, 478–486. [[CrossRef](#)]
31. Wu, J.M.; Yang, Y.F.; Chen, J.L. Study on the causes of catalyst inactivation of benzene semi-hydrogenation. *Chem. Ind. Eng. Prog.* **2003**, *22*, 295–297.
32. Sun, H.J.; Qin, H.A.; Huang, Z.X.; Su, M.F.; Li, Y.Y.; Liu, S.C.; Liu, Z.Y. Effect of reaction modifier ZnSO₄ and pretreatment on performance of Ru-Zn catalyst for selective hydrogenation of benzene to cyclohexene. *Chin. J. Inorg. Chem.* **2017**, *33*, 73–80.
33. Struijk, J.; d'Angremond, M.; Lucas-de Regt, W.J.M.; Scholten, J.J.F. Partial liquid phase hydrogenation of benzene to cyclohexene over ruthenium catalysts in the presence of an aqueous salt solution I. Preparation, characterization of the catalyst and study of a number of process variables. *Appl. Catal. A Gen.* **1992**, *83*, 263–295. [[CrossRef](#)]
34. Ramírez, A.; Hillebrand, P.; Stellmach, D.; May, M.M.; Bogdanoff, P.; Fiechter, S. Evaluation of MnO_x, Mn₂O₃, and Mn₃O₄ electrodeposited films for the oxygen evolution reaction of water. *J. Phys. Chem. C* **2014**, *118*, 14073–14081. [[CrossRef](#)]
35. Reddy, A.S.; Kim, J. An efficient g-C₃N₄-decorated CdS-nanoparticle-doped Fe₃O₄ hybrid catalyst for an enhanced H₂ evolution through photoelectrochemical water splitting. *Appl. Surf. Sci.* **2020**, *513*, 145836. [[CrossRef](#)]
36. Kötz, R.; Lewerenz, H.J.; Stucki, S. XPS Studies of Oxygen Evolution on Ru and RuO₂ Anodes. *J. Electrochem. Soc.* **1983**, *130*, 825–828. [[CrossRef](#)]
37. Mazzieri, V.A.; L'Argentière, P.C.; Coloma-Pascual, F.; Fígoli, N.S. Effect of Chlorine on the Properties of Ru/Al₂O₃. *Ind. Eng. Chem. Res.* **2003**, *42*, 2269–2272. [[CrossRef](#)]

